Adducts of the Lewis acid [B(C₆F₅)₃] with transition metal oxo compounds

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The oxo anions $[WO_4]^{2-}$ and $[ReO_4]^-$ react with the Lewis acid molecule $[B(C_6F_5)_3]$ to give the tris-adduct $[WO\{OB(C_6F_5)_3\}_3]^{2-}$ or the mono adduct $[ReO_3\{OB(C_6F_5)_3\}]^-$ respectively. The crystal structure of the salt $[^nPr_4N]_2[WO\{OB(C_6F_5)_3\}_3]$ has been determined. The η-cyclopentadienyl-oxo compounds $[Re(\eta\text{-}C_5R_5)O_3]$ (where R = H or Me) react with $[B(C_6F_5)_3]$ giving the mono adducts $[(\eta\text{-}C_5R_5)ReO_2\{OB(C_6F_5)_3\}]$ and the crystal structure of the compound where R = H has been determined. The triazacyclononane compounds $[LMO_3]$ (where L = N,N',N''-trimethyl-1,4,7-triazacyclononane and M = Mo or W) with $[B(C_6F_5)_3]$ give the mono adducts $[LMO_2\{OB(C_6F_5)_3\}]$ and the crystal structure of the tungsten compound is reported. The compound $[Re\{HB(pz)_3\}O_3]$ [where $\{HB(pz)_3\}$ = hydridotris(1-pyrazolyl) borate] and $[B(C_6F_5)_3]$ gives the mono adduct $[HB(pz)_3ReO_2\{OB(C_6F_5)_3\}]$.

The Lewis acid $[B(C_6F_5)_3]$ is readily available as thermally stable volatile white crystals which are soluble in toluene. The solutions react only slowly with water and oxygen. Therefore, compared with the very volatile BF_3 (bp $-99.9\,°C$), which rapidly hydrolyses giving HF, the Lewis acid $[B(C_6F_5)_3]$ is much more convenient for the exploration of the Lewis base properties of transition metal compounds. Adducts formed between $[B(C_6F_5)_3]$ and metal-alkyl[1,2,3] metal-hydrido[4] and metal-oxo compounds[5–8] are now well established. In this work we describe further the Lewis base properties of some neutral and anionic transition metal-oxo compounds.

Results and discussion

Treatment of the oxo compound $[^nPr_4N]_2[WO_4]$ in CH_2Cl_2 solution with three equivalents of $[B(C_6F_5)_3]$ gave the compound $[^nPr_4N]_2[WO\{OB(C_6F_5)_3\}_3]$ **1** as white, microcrystalline, air-stable crystals in good yield. The compound **1** is very soluble in CH_2Cl_2, slightly soluble in toluene and insoluble in light petroleum ether and pentane. It has been characterised by IR and NMR (^{11}B, ^{1}H, ^{13}C, ^{19}F) spectroscopies, elemental analysis and X-ray diffraction. The analytical and selected spectroscopic data are given in Table 1 for compound **1** and the other new compounds **2–10**.

Crystals of **1** suitable for X-ray diffraction studies were grown from CH_2Cl_2/light petroleum ether (bp 30–40 °C). Selected distances and angles are given in Table 2 and the structure of the anion is shown in Fig. 1. The oxygen atoms attached to the tungsten have a slightly distorted tetrahedral geometry. The W–O–B units adopt a nearly linear disposition with angles 174.5(2), 174.4(1) and 170.1(1)°. The four W–O distances are within the range found for W–O bonds in the compound $[^tBuNH_3][WO_4]$ (1.60(6)–1.81(2) Å),[9] but the three W–O distances of the atoms bonded to boron (1.781(2), 1.785(1), and 1.786(1) Å) are 0.07 Å longer than the distance to the uncoordinated oxygen atom (1.714(2) Å). The lengthening of the M–O bond in the W–O–B systems is of the same order as those reported for the M–O–B systems in the compounds $[Ti\{OB(C_6F_5)_3\}(acac)_2]$, $[V\{OB(C_6F_5)_3\}(acac)_2]$, $[MoO\{OB(C_6F_5)_3\}(acac)_2]$,[6] $[V(OBPh_3)(C_{22}H_{22}N_4)]$[10] and $[(C_9H_{21}N_3)WO_2(OBPh_3)]$.[11] The O–B distances in **1** are 1.491(3), 1.508(3) and 1.494(3) Å and they lie in the range of O–B distances for
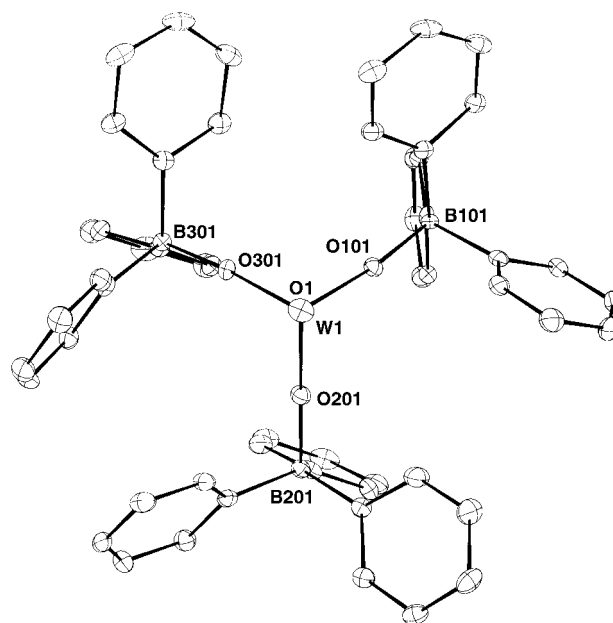

Fig. 1 Crystal structure of **1**, $[^nPr_4N]_2[WO\{OB(C_6F_5)_3\}_3]$, with a view along the W=O bond and fluorine atoms removed for clarity.

other M–O–B adducts (from 1.460(6) in $[(Me_5Cp)_2ZrOB(C_6F_5)_3]$[5] to 1.59(3) Å in $[(C_9H_{21}N_3)WO_2(OBPh_3)]$[11,12].

The ^{11}B NMR spectrum of **1** shows a very broad peak at $\delta = 1$, well within the range of a tetra-coordinated boron species and in the region of the other known M–O–B adducts.[5,6,13] It was not possible to identify the W=O absorption band in the IR spectrum because $[B(C_6F_5)_3]$ absorbs strongly in the same region as M=O bonds. When $[Pr_4N]_2[WO_4]$ was reacted with one, two or four equivalents of $[B(C_6F_5)_3]$ the ^{11}B NMR spectra of these solutions show the broad peak around 1 ppm indicating that a metal-oxo Lewis acid adduct has formed. The reaction of $[^nPr_4N]_2[WO_4]$ with one equivalent of the Lewis acid led to the formation of a colourless oil that could not be fully characterised, but the reaction with 2–4 equivalents of $[B(C_6F_5)_3]$ yields only $[^nPr_4N]_2[WO\{OB(C_6F_5)_3\}_3]$ **1**, as white crystals.

Table 1 Analytical and spectrscopic data

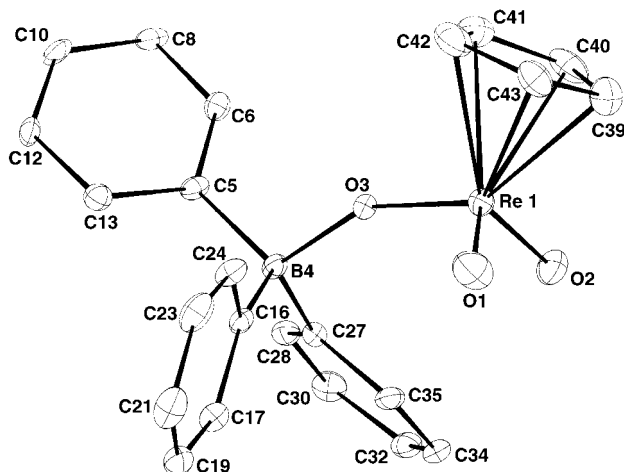| Compound and analysis[a]	NMR data[b] (ppm)
[nPr₄N]₂[WO{OB(C₆F₅)₃}₃]·0.5CH₂Cl₂ **1** White C (42.9) 42.9 H (2.6) 2.4 N (1.3) 1.3 B (1.5) 1.4 W (8.4) 8.2	^{1}H: 0.96 [t (7), 24H, NCH₂CH₂CH₃], 1.63 [m, 16H, NCH₂CH₂CH₃], 2.99 [m, 16H, NCH₂CH₂CH₃] ^{13}C: 148.0 [d (240), C₆F₅], 139.3 [d (246), C₆F₅], 136.8 [d (246), C₆F₅], 121.7 [s, C₆F₅], 60.8 [s, NCH₂-CH₂CH₃], 15.5 [s, NCH₂CH₂CH₃], 10.1 [s, NCH₂CH₂CH₃] ^{19}F: −140.5 [d (19), C₆F₅], −167.7 [t (19), C₆F₅], −172.9 [dd (19, 19), C₆F₅] ^{11}B: 1.0 very broad
[nBu₄N]₂[WO{OB(C₆F₅)₃}₃] **2** Colorless oil C (45.5) 45.5 H (3.2) 3.35 N (1.2) 1.2 B (1.4) 1.4 W (8.1) 9.8	^{1}H: 0.96 [t (7), 24H, NCH₂CH₂CH₂CH₃], 1.35 [m, 16H, NCH₂CH₂CH₂CH₃], 1.58 [m, 16H, NCH₂-CH₂CH₂CH₃], 2.99 [m, 16H, NCH₂CH₂CH₂CH₃] ^{13}C: 146.6 [d (251), C₆F₅], 139.0 [d (254), C₆F₅], 136.4 [d (250), C₆F₅], 58.7 [s, NCH₂CH₂CH₂CH₃], 23.5 [s, NCH₂CH₂CH₂CH₃], 19.3 [s, NCH₂CH₂CH₂CH₃], 12.6 [s, NCH₂CH₂CH₂CH₃] ^{11}B: 0.4 broad
[nPr₄N][ReO₃{OB(C₆F₅)₃}] **3** White C (38.0) 37.4 H (3.0) 3.7 N (1.5) 1.65 B (1.1) 0.9 Re (19.6) 20.5	^{1}H: 1.04 [t (7), 12H, NCH₂CH₂CH₃], 1.70 [m, 8H, NCH₂CH₂CH₃], 3.09 [m, 8H, NCH₂CH₂CH₃] ^{13}C: 147.7 [d (234), C₆F₅], 140.0 [d (204), C₆F₅], 137.1 [d (234), C₆F₅], 60.5 [s, NCH₂CH₂CH₃], 15.5 [s, NCH₂CH₂CH₃], 10.1 [s, NCH₂CH₂CH₃] ^{19}F: −137.8 [dd (24, 9) C₆F₅], −162.9 [t (21), C₆F₅], −168.7 [ddd (24, 21, 7), C₆F₅ ^{11}B: 3.1
[PhCH₂Ph₃P][ReO₃{OB(C₆F₅)₃}] **4** White C (46.3) 46.8 H (2.0) 1.73 B (0.97) 0.8 Re (16.7) 18.5	^{1}H: 7.84–6.48 [m, 20H, Ph], 4.47 [d (14), 2H, CH₂] ^{13}C: 148.0 [d (242), C₆F₅], 138.9 [d (189), C₆F₅], 136.8 [d (261), C₆F₅], 135.8–116.4 [m, Ph], 31.8 [d (45), PhCH₂P] ^{19}F: −134.5 [dd (24, 9), C₆F₅], −159.8 [t (20), C₆F₅], −165.4 [ddd (24, 20, 8), C₆F₅] ^{11}B: 3.0 s ^{31}P: 19.1 s
[Ph₄P][ReO₃{OB(C₆F₅)₃}] **5** White C (45.8) 45.9 H (1.8) 1.4 B (1.0) 0.8 Re (16.9) 19.0	^{1}H: 7.91–6.58 [m, 20H, Ph] ^{13}C: 148.0 [d (242), C₆F₅], 139.7 [d (246), C₆F₅], 137.3 [d (219), C₆F₅], 135.8–117.3 [m, Ph] ^{19}F: 2.7 s ^{31}P: 20.5 s ^{11}B: 3.3 s
[Re(η-C₅H₅)O₂{OB(C₆F₅)₃}] **6** Yellow C (34.05) 34.2 H (0.6) 0.4 B (1.3) 1.0 Re (22.95) 22.9	^{1}H: 7.12 [s, 5H, C₅H₅] ^{13}C: 149.2 [s, C₆F₅], 141.8 [s, C₆F₅], 138.7 [s, C₆F₅], 117.6 [s, C₆F₅], 116.1 [s, C₅H₅] ^{19}F: −145.7 [s, C₆F₅], −157.8 [s, C₆F₅], −164.9 [s, C₆F₅] ^{11}B: 5.2 s
[Re(η-C₅Me₅)O₂{OB(C₆F₅)₃}] **7** Orange C (38.2) 38.3 H (1.7) 2.0 B (1.2) 1.0 Re (21.1) 21.0	^{1}H: 2.21 [s, 15H, C₅Me₅] ^{13}C: 148.0 [d (234), C₆F₅], 139.2 [d (364), C₆F₅], 136.2 [d (85), C₆F₅], 122.9 [s, C₅Me₅], 119.7 [s, C₆F₅], 10.3 [s, C₅Me₅] ^{19}F: −133.6 [s, C₆F₅], −156.5 [s, C₆F₅], −165.1 [s, C₆F₅] ^{11}B: −2.0 s
[LMoO₂{OB(C₆F₅)₃}]·0.5CH₂Cl₂ **8** White C (38.0) 37.4 H (2.55) 2.8 B (1.2) 1.4 Mo (11.0) 11.55 N (4.8) 4.1	^{1}H: 3.15 [s, 9H, CH₃], 2.91 [s, 12H, CH₂] ^{19}F: −135.1 [d (25), C₆F₅], −164.2 [t (19), C₆F₅], −169.3 [dd (25, 19), C₆F₅] ^{11}B: 1.1 s
[LWO₂{OB(C₆F₅)₃}]·0.5CH₂Cl₂ **9** White C (34.5) 34.4 H (2.3) 2.3 N (4.4) 4.7 B (1.1) 1.2 W (17.7) 23.0	^{1}H: 3.27 [m, 9H, CH₃], 2.99 [m, 12H, CH₂] ^{13}C: 148.2 [s, C₆F₅], 139.4 [s, C₆F₅], 137.1 [s, C₆F₅] ^{19}F: −131.6 [d (23), C₆F₅], −161.0 [t (21), C₆F₅], −166.1 [dd (23, 21), C₆F₅] ^{11}B: 0.3 s
[{HB(pz)₃}ReO₂{OB(C₆F₅)₃}] **10** Yellow C (33.8) 33.9 H (1.05) 1.6 N (8.8) 8.2 B (2.25) 1.9 Re (19.4) 19.2	^{1}H: 8.17 [s, 1H, CH], 7.79 [s, 1H, CH], 6.35 [s, 1H, CH] ^{19}F: −134.9 [s, C₆F₅], −156.6 [s, C₆F₅], −164.0 [s, C₆F₅] ^{11}B: −4.9 s

[a] Given as (found) calc. %. [b] All NMR spectra were measured in CD₂Cl₂.

The treatment of [nBu₄N]₂[WO₄] with one, two, three, or four equivalents of [B(C₆F₅)₃] gives oils. After many attempts a few crystals were obtained and the elemental analysis was consistent with the formula [nBu₄N]₂[WO{O₃B(C₆F₅)₃}₃] **2**. The ^{11}B NMR spectrum of **2** shows a broad peak at δ 0.4 which is consistent with the formation of a tris-adduct.

The salts of the perrhenate anion C⁺[ReO₄]⁻, where C = nPr₄N, (PhCH₂)Ph₃P or Ph₄P, react with [B(C₆F₅)₃] to give the mono adducts [C][ReO₃{OB(C₆F₅)₃}], where C = nPr₄N **3**, (PhCH₂)Ph₃P **4** or Ph₄P **5**, as white air-stable crystalline solids. These salts are very soluble in CH₂Cl₂, but insoluble in light petroleum ether, pentane or toluene. Despite many attempts

Table 2 Selected distances (Å) and angles (°) for the compound [nPr₄N]₂[WO{OB(C₆F₅)₃}₃], **1**

W(1)–O(1)	1.714(2)	O(1)–W(1)–O(10)	110.06(8)
W(1)–O(101)	1.786(1)	O(101)–W(1)–O(201)	111.16(7)
W(1)–O(201)	1.785(1)	O(1)–W(1)–O(201)	108.12(8)
W(1)–O(301)	1.781(2)	O(101)–W(1)–O(301)	109.29(7)
O(101)–B(101)	1.491(3)	O(1)–W(1)–O(301)	108.90(7)
O(201)–B(201)	1.508(3)	O(201)–W(1)–O(301)	109.28(7)
O(301)–B(301)	1.494(3)	W(1)–O(101)–B(101)	170.1(1)
		W(1)–O(201)–B(201)	174.4(1)
		W(1)–O(301)–B(301)	174.5(2)

Table 3 Selected distances (Å) and angles (°) for [Re(η-C₅H₅)O₂{OB(C₆F₅)₃}], **6**

Re(1)–O(1)	1.708(4)	O(1)–Re(1)–O(2)	104.9(2)
Re(1)–O(2)	1.705(3)	O(2)–Re(1)–O(3)	105.4(2)
Re(1)–O(3)	1.775(3)	O(1)–Re(1)–O(3)	104.4(2)
O(3)–B(4)	1.568(5)	Re(1)–O(3)–B(4)	149.4(2)

Table 4 Selected distances (Å) and angles (°) for the compound [LWO₂{OB(C₆F₅)₃}], **9**

Molecule 1 in asymmetric unit		Molecule 2 in asymmetric unit	
W(1)–O(2)	1.850(3)	W(39)–O(40)	1.853(3)
W(1)–O(37)	1.708(3)	W(39)–O(75)	1.720(3)
W(1)–O(38)	1.719(3)	W(39)–O(76)	1.770(3)
W(1)–N(97)	2.357(4)	W(39)–N(83)	2.298(4)
W(1)–N(101)	2.334(4)	W(39)–N(87)	2.329(4)
W(1)–N(104)	2.384(4)	W(39)–N(90)	2.290(3)
O(2)–B(3)	1.499(5)	O(40)–B(41)	1.513(5)
O(2)–W(1)–O(37)	107.6(1)	O(40)–W(39)–O(76)	104.3(1)
O(2)–W(1)–O(38)	104.6(1)	O(75)–W(39)–O(76)	103.9(2)
O(37)–W(1)–O(38)	106.7(2)	O(40)–W(39)–O(75)	103.9(1)
W(1)–O(2)–B(3)	140.6(3)	W(39)–O(40)–B(41)	141.5(3)

Fig. 2 Crystal structure of **6**, [Re(η-C₅H₅)O₂{OB(C₆F₅)₃}], with fluorine atoms removed for clarity.

it was not possible to grow crystals of **3**–**5** suitable for single-crystal X-ray diffraction. The NMR and IR spectra and elemental analyses of **3**–**5** support the proposed formulation of the products as the mono adducts. The ¹¹B chemical shifts (3.1, 3.0 and 3.3 ppm respectively) are in the region expected for tetra-coordinated boron and inside the range for M–O–B adducts.[5,6,13] The presence of the [B(C₆F₅)₃] group is confirmed by ¹⁹F and ¹³C NMR spectra and by an IR spectrum. Treatment of the mono anion [ReO₄]⁻ with an excess of [B(C₆F₅)₃] gives only the mono adduct.

Treatment of the oxo-complexes [Re(η-C₅R₅)O₃] (where R = H or Me) with [B(C₆F₅)₃] gives the mono adducts [(η-C₅R₅)-ReO₂{OB(C₆F₅)₃}] (where R = H **6** or R = Me **7**) as air stable yellow and orange crystalline solids respectively. Both **6** and **7** are very soluble in CH₂Cl₂; **6** is insoluble in light petroleum ether, but **7** is slightly soluble. The compounds [Re(η-C₅R₅)O₃] with an excess of [B(C₆F₅)₃] give only the mono adducts.

The spectroscopic data and elemental analysis support the proposed formulation and the crystal structure of **6** has been determined. The structure of **6** is shown in Fig. 2 and selected distances and angles are given in Table 3. The Re=O distances of the terminal Re=O groups are 1.708(4) and 1.705(3) Å and these are similar to the values for the Re=O bonds in the starting compound[14] and also the related compounds [Re(η-C₅H₄Me)O₃][15] and [Re(η-C₅Me₄Et)O₃].[16] The Re–O distance in the Re–O–B system is 0.07 Å longer, as expected. The O–B distance is in the range for other known M–O–B adducts.[5,6,9,11,13] The W–O–B units in **1** show a linear disposition (174.5(2), 174.4(1) and 170.1(1)°), but in [(η-C₅R₅)-ReO₂{OB(C₆F₅)₃}] the unit has a bent arrangement (149.4(2)°). The M–O–B groups in the related compounds are also linear[6,12,17] or bent.[5,10,11]

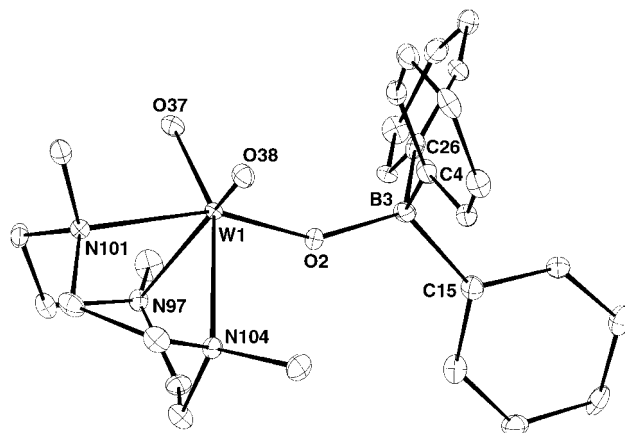Treatment of the triazacyclononane compounds [LMO₃] (where L = N,N′,N″-trimethyl-1,4,7-triazacyclononane and M = Mo or W) with [B(C₆F₅)₃] gives the mono adducts [LMO₂-{OB(C₆F₅)₃}], (where M = Mo **8**, W **9**) in good yields as white crystalline, air-stable solids. The compounds **8** and **9** are slightly

Fig. 3 Crystal structure of one molecule of **9**, [LWO₂{OB(C₆F₅)₃}], from the asymmetric unit, with fluorine atoms removed for clarity.

soluble in CH₂Cl₂, or hot toluene and insoluble in light petroleum ether or pentane. Reactions with an excess of [B(C₆F₅)₃] yield only the mono adducts. The compounds **8** and **9** have been characterised by NMR and IR spectroscopy and elemental analysis. Due to their low solubility it was not possible to obtain satisfactory ¹³C NMR spectra. The ¹¹B NMR spectra show resonances in the region expected for tetra-coordinated boron at 1.1 ppm for **8** and at 0.25 ppm for **9**.

The crystal structure of **9** has been determined. There are two molecules in the asymmetric unit, but the distances and angles of each are nearly identical. The structure of one molecule is shown in Fig. 3 and selected distances and angles are given in Table 4. The W–O distances of the uncoordinated oxygen atoms (average 1.721 Å) are 0.12 Å longer than the W–O distance of the coordinated oxygen (average 1.852 Å), in agreement with the expected lengthening of a metal oxygen bond upon coordination of the oxygen to the boron.[6,10,11] The B–O distance (average 1.506 Å) lies in the range of the other known M–O–B moieties[5,11] and the M–O–B unit adopts a bent disposition (average 141.1°). The closely related compound [LWO₂(OBPh₃)][11] also has a bent disposition (154.2(10)°). The W–O distance of the coordinated oxygen is slightly longer (0.07 Å) in **9** than in [LWO₂(OBPh₃)] and the O–B distance is slightly shorter (0.08 Å). This can be attributed to [B(C₆F₅)₃] being a stronger Lewis acid than BPh₃.

When the colourless compounds [Re{HB(pz)$_3$}O$_3$] (where {HB(pz)$_3$} = hydridotris(1-pyrazolyl)borate) and [B(C$_6$F$_5$)$_3$] are mixed in CH$_2$Cl$_2$ the solution immediately becomes yellow and the compound [HB(pz)$_3$ReO$_2${OB(C$_6$F$_5$)$_3$}], **10**, can be isolated as yellow crystals. It has been characterised by NMR studies and elemental analysis. Instead of the two expected peaks, one for the pyrazolylborate ligand and the other for the Lewis acid, the ^{11}B NMR spectrum shows a single broad peak at −4.9 ppm due to both ligands. The peak is rather broad so it seems that the two signals overlap, since the presence of the {HB(pz)$_3$} ligand is confirmed by the ^{1}H NMR spectrum which shows three singlets at 8.17, 7.79 and 6.35 ppm. The ^{19}F NMR spectrum clearly shows the three resonances with chemical shifts of −134.9, −156.6 and −164.0 ppm typical of [B(C$_6$F$_5$)$_3$] adducts. In addition the elemental analysis supports the proposed formula. Due to the low stability of the compound it was not possible to record the ^{13}C NMR spectrum or grow crystals of good quality for X-ray diffraction. In about 2 hours the solutions of **10** became colourless even when kept at −20 °C. In the solid state under nitrogen, it decomposed in a week.

In conclusion, the synthesis and the structures proposed for the new compounds are shown in Scheme 1. The greater basicity of the dianion [WO$_4$]$^{2-}$ compared to the mono anion [ReO$_4$]$^-$ is manifested by formation of the tris-adduct by the tungstate anion compared to the mono-adduct formed with the perrhenate anion. The formation of these adducts with the metal-oxo anions suggests there can be an extensive chemistry of related oxo-anion adducts.

Experimental

All manipulations were carried out under an N$_2$ atmosphere by using standard Schlenk or dry-box techniques. Light petroleum ether (bp 40–60 °C), pentane, toluene, and dichloromethane were dried over suitable reagents and distilled under N$_2$. The compounds [^{n}Bu$_4$N]$_2$[WO$_4$], [Re(η-C$_5$H$_5$)O$_3$], [Re(η-C$_5$Me$_5$)O$_3$], [LWO$_3$] (where L = N,N',N''-trimethyl-1,4,7-triazacyclononane, M = Mo, W), [Re{HB(pz)$_3$}O$_3$] [{HB(pz)$_3$} = hydridotris(1-pyrazolyl)borate] and [B(C$_6$F$_5$)$_3$] were prepared as described.[14,18–22]

NMR spectra were recorded using a Bruker WM 300 spectrometer for ^{1}H, ^{13}C, ^{11}B and ^{31}P at 300, 75.5, 96 and 121.5 MHz respectively or a Varian AM 500 for ^{1}H, ^{13}C, ^{11}B and ^{19}F at 500, 125.7, 160 and 470 MHz respectively. The ^{1}H and ^{13}C chemical shifts are reported with respect to SiMe$_4$, ^{11}B to BF$_3$·OEt$_3$, ^{19}F to CHF$_3$ and ^{31}P to trimethyl phosphate in D$_2$O. Chemical shifts are given in ppm, a positive sign indicates a down field shift relative to the standard, and coupling constants in Hz. Infrared spectra were recorded as KBr discs in a Perkin-Elmer FT 1710 spectrometer, mass spectra by the EPSRC National Mass Spectrometry Service Centre. Elemental analyses were obtained by the analytical department of this laboratory.

Syntheses

[^{n}Pr$_4$N]$_2$[WO{OB(C$_6$F$_5$)$_3$}$_3$] **1**. The compound [^{n}Pr$_4$N]$_2$[WO$_4$] was prepared as described for [^{n}Bu$_4$N]$_2$[WO$_4$][18] using ^{n}Pr$_4$NOH instead of ^{n}Bu$_4$NOH. A mixture of [^{n}Pr$_4$N]$_2$[WO$_4$] (200 mg, 0.32 mmol) and [B(C$_6$F$_5$)$_3$] (495 mg, 0.97 mmol) was stirred in CH$_2$Cl$_2$ (20 ml) for 1 h. The colourless solution was filtered and the filtrate was concentrated to *ca.* 10 ml and then layered with light petroleum ether (10 ml) and cooled to −20 °C. Small colourless crystals were obtained after 48 h. Yield: 503 mg, 72%.

[^{n}Bu$_4$N]$_2$[WO{OB(C$_6$F$_5$)$_3$}$_3$] **2**. A mixture of [^{n}Bu$_4$N]$_2$[WO$_4$][18] (200 mg, 0.27 mmol) and [B(C$_6$F$_5$)$_3$] (420 mg, 0.82 mmol) was stirred in CH$_2$Cl$_2$ (20 ml) for 1 h. The solution was filtered and the solvent removed in vacuo to give a colourless oil.
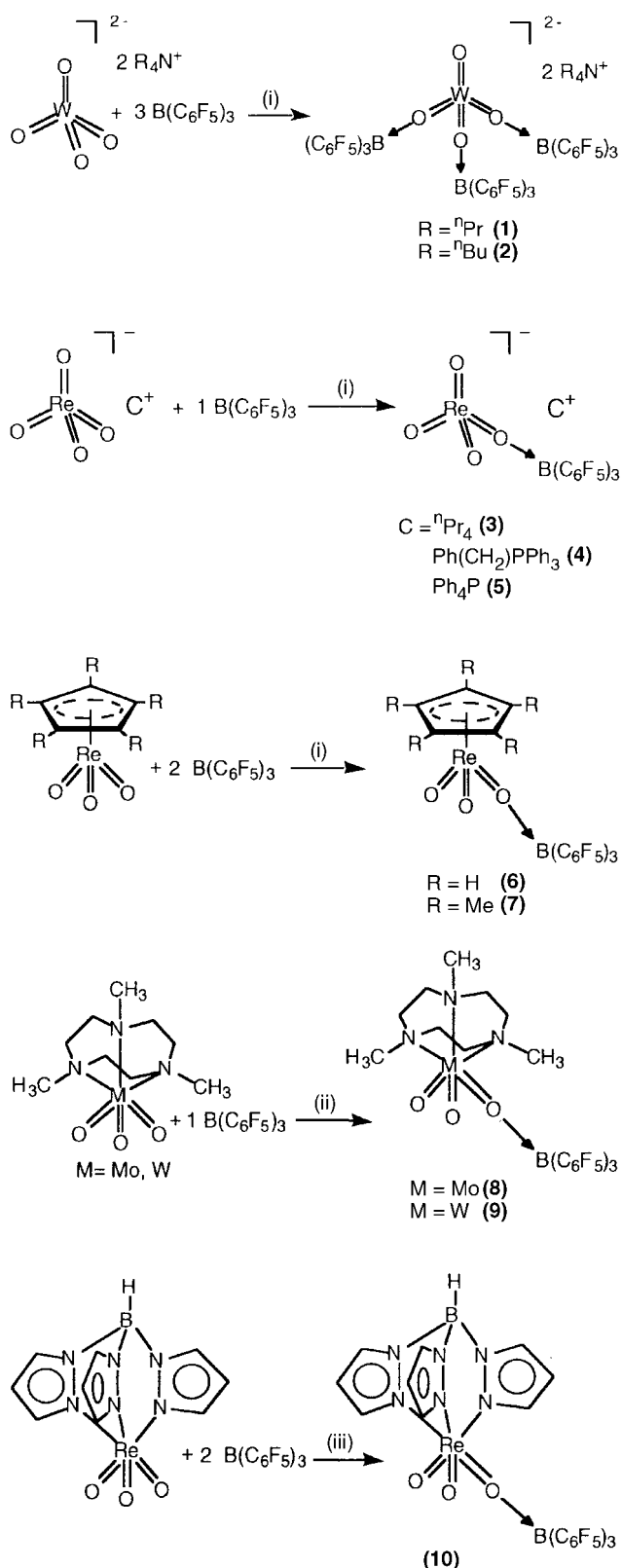
Scheme 1 (i) In CH$_2$Cl$_2$ at room temperature for 1 h. (ii) In CH$_2$Cl$_2$ at room temperature for 1.5 h for **8** and reflux in CH$_2$Cl$_2$ for 4 h for **9**. (iii) In CH$_2$Cl$_2$ at room temperature for 15 min.

[C][ReO$_4$] (C = ^{n}Pr$_4$N, (PhCH$_2$)Ph$_3$P, Ph$_4$P). The compounds [C][ReO$_4$] (C = ^{n}Pr$_4$N, (PhCH$_2$)Ph$_3$P, Ph$_4$P) were prepared by addition of a solution of ^{n}Pr$_4$NOH, PhCH$_2$Ph$_3$PCl or Ph$_4$PCl in water to a solution of NH$_4$ReO$_4$ in water. In each case there was an immediate formation of a white precipitate. These precipitates were collected by filtration, washed with water and dried in vacuo. These products were used without further purification or characterisation.

Table 5 Crystallographic collection and processing parameters for compounds **1**, **6** and **9**

	$[^nPr_4N]_2[WO\{OB(C_6F_5)_3\}_3]$ **1**	$[(\eta-C_5H_5)ReO_2\{OB(C_6F_5)_3\}]$ **6**	$[LWO_2\{OB(C_6F_5)_3\}]$ **9**
Molecular formula	$C_{78}H_{56}WO_4B_3F_{45}N_2$	$C_{23}H_5ReO_3BF_{15}$	$C_{56}H_{46}W_2O_6B_2F_{30}Cl_4N_6$
Formula weight	2156.51	811.27	2000.10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1$
$a/Å$	16.157(1)	11.300(1)	13.289(1)
$b/Å$	21.204(1)	9.585(1)	14.028(1)
$c/Å$	23.912(1)	20.596(1)	18.270(1)
$\beta/°$	92.731(2)	90.648(2)	110.256(3)
Unit-cell volume/$Å^3$	8182.78	2230.62	3195.22
Formula units per cell, Z	4	4	2
$\rho_{calc}/g\ cm^{-3}$	1.75	2.42	2.08
$\mu(Mo-K\alpha)/mm^{-1}$	1.59	5.67	3.98
T/K	100	100	100
Crystal size/mm	$0.21 \times 0.23 \times 0.32$	$0.25 \times 0.15 \times 0.05$	$0.20 \times 0.15 \times 0.10$
$\theta_{max}/°$	26.69	26.72	26.69
No. of reflections:			
total	58107	14286	22644
unique	16848	4469	6588
in refinement $[I > 3\sigma(I)]$	14377	3989	6496
No. of variables	1198	388	956
Residual electron density			
minimum	-0.42	-1.80	-0.92
maximum	0.98	1.80	0.73
R	0.0303	0.0346	0.0189
R_w	0.0301	0.0362	0.0220

$[^nPr_4N][ReO_3\{OB(C_6F_5)_3\}]$ 3. A mixture of $[^nPr_4N][ReO_4]$ (200 mg, 0.2 mmol) and $[B(C_6F_5)_3]$ (234 mg, 0.4 mmol) was stirred in CH_2Cl_2 (20 ml) for 1 h. The colourless solution was filtered, the solvent removed in vacuum giving a white solid which was washed with light petroleum ether (2×10 ml) to yield a white solid. Yield: 365 mg, 81%.

$[(PhCH_2)Ph_3P][ReO_3\{OB(C_6F_5)_3\}]$ 4. A mixture of $[(PhCH_2)-Ph_3P][ReO_4]$ (300 mg, 0.5 mmol) and $[B(C_6F_5)_3]$ (254 mg, 0.5 mmol) was stirred in CH_2Cl_2 (25 ml) for 1 h. The solution was filtered and the solvent removed from the filtrate under reduced pressure. The white residue was washed with pentane (2×10 ml) to yield a white solid. Yield: 402 mg, 73%.

$[Ph_4P][ReO_3\{OB(C_6F_5)_3\}]$ 5. $[Ph_4P][ReO_3\{OB(C_6F_5)_3\}]$ was prepared as a white solid as described for **4** from $[Ph_4P][ReO_4]$ (200 mg, 0.39 mmol) and $[B(C_6F_5)_3]$ (174 mg, 0.34 mmol). Yield: 287 mg, 78%.

$[(\eta-C_5H_5)ReO_2\{OB(C_6F_5)_3\}]$ 6. A solution of $[B(C_6F_5)_3]$ (171 mg, 0.33 mmol) in CH_2Cl_2 (5 ml) was added with stirring to a solution of $[Re(\eta-C_5H_5)O_3]$ (50 mg, 0.17 mmol) in CH_2Cl_2 (10 ml). The reaction mixture was stirred for 1 h. The resulting yellow-orange solution was filtered and concentrated to *ca.* 5 ml, then the solution was layered with light petroleum ether (5 ml) and stored at $-20\ °C$ overnight giving yellow crystals. Yield: 102 mg, 76%.

$[(\eta-C_5Me_5)ReO_2\{OB(C_6F_5)_3\}]$ 7. The compound was prepared as described for $[(\eta-C_5H_5)ReO_2\{OB(C_6F_5)_3\}]$ **6** using $[Re(\eta-C_5Me_5)O_3]$ (50 mg, 0.14 mmol) and $[B(C_6F_5)_3]$ (138 mg, 0.28 mmol), after three days at $-20\ °C$ red-orange crystals were obtained. Concentration of the mother liquor afforded another crop. Yield: 87 mg, 73%.

$[LMoO_2\{OB(C_6F_5)_3\}]$ 8. A solution of $[B(C_6F_5)_3]$ (244 mg, 0.48 mmol) in CH_2Cl_2 (10 ml) was added with stirring to a suspension of $[LMoO_3]$ (150 mg, 0.48 mmol) in CH_2Cl_2 (10 ml). The reaction mixture was stirred for 1.5 h at room temperature. The resulting colourless solution was filtered and the solvent was removed under reduced pressure giving an oily solid. This was washed with light petroleum ether (2×5 ml) to give a white solid. Yield: 290 mg, 74%.

$[LWO_2\{OB(C_6F_5)_3\}]\cdot0.5CH_2Cl_2$ 9. A solution of $[B(C_6F_5)_3]$ (190 mg, 0.37 mmol) in CH_2Cl_2 (5 ml) was added with stirring to a suspension of $[LWO_3]$ (150 mg, 0.37 mmol) in CH_2Cl_2 (10 ml) at room temperature. The reaction mixture was then refluxed for 4 h. The resulting colourless solution was filtered and the solvent was removed using reduced pressure giving an oily solid. The residue was washed with light petroleum ether (2×5 ml) giving a white solid. Yield: 220 mg, 65%.

$[\{HB(pz)_3\}ReO_2\{OB(C_6F_5)_3\}]$ 10. A mixture of $[\{HB(pz)_3\}-ReO_3]$ (50 mg, 0.11 mmol) and $[B(C_6F_5)_3]$ (115 mg, 0.22 mmol) was dissolved in CH_2Cl_2 (15 ml) and stirred for 15 min, then the yellow solution was filtered and concentrated to half volume, light petroleum ether (10 ml) was added and the solution was concentrated under reduced pressure until a crystalline yellow solid was formed. The solid was filtered, washed with light petroleum ether (2×5ml) and dried in vacuum. Yield: 77 mg, 72%.

Crystal structure determination

Crystals of the compounds $[^nPr_4N]_2[WO\{OB(C_6F_5)_3\}_3]$, **1**, $[(\eta-C_5H_5)ReO_2\{OB(C_6F_5)_3\}]$, **6**, and $[LWO_2\{OB(C_6F_5)_3\}]$, **9**, were grown by slow diffusion of light petroleum ether into saturated solutions of the complexes in CH_2Cl_2 at $-20\ °C$. The selected crystals were mounted on a nylon fibre using a drop of perfluoropolyether oil. They were rapidly cooled to 100 K in a flow of cold nitrogen using an Oxford Cryosystems CRYO-STREAM cooling system. The crystal data are given in Table 5. The data were collected on an Enraf–Nonius DIP2020 image-plate diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). The images were processed using the DENZO and SCALEPACK suite of programs.[23] Data were corrected for Lorentz and polarisation effects and a partial absorption correction applied by multi-frame scaling of the image-plate data using equivalent reflections. Structures were solved by direct methods, SIR92,[24] giving all non-hydrogen atom positions, and refined using full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed in calculated positions during the final cycles of refinement. A three parameter Chebychev weighting scheme[25] and corrections for anomalous dispersion were applied to all data. All

crystallographic calculations were carried out using CRYS-TALS[26] on a PC/AT computer. Neutral atom scattering factors were taken from reference 27.

CCDC reference number 186/1355.

See http://www.rsc.org/suppdata/dt/1999/1061/ for crystallographic files in .cif format.

Acknowledgements

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